

INTRODUCING FUNCTIONALITY BY GRAPHENE COVALENT GRAFTING

KOVAŘÍČEK Petr, KALBÁČ Martin

J. Heyrovsky Institute of Physical Chemistry of the Academy of Sciences of the Czech Republic, Prague, Czech Republic, EU

Abstract

Graphene is a material of great potential in a broad range of applications, for each of which specific tuning of the material's properties is required. This can be achieved, for example, by covalent functionalization. We have exploited protocols for surface grafting by diazonium salts, by nucleophilic and electrophilic substitution to perform graphene covalent modification of graphene on substrates. The painstaking analysis problem of monolayered materials was addressed using Raman spectroscopy, SERS, SEIRA, MS, AFM, XPS and SEM/EDX. The covalent grafting was shown to tolerate the transfer process, thus allowing ex post transfer from copper to other substrates. Functional devices often require combination of several materials with specific functions, such as graphene-polymer hybrid heterostructures. We have used the developed methodology of chemical functionalization for preparation of PEDOT:Graphene bilayers by selective in situ polymerization of EDOT on covalently functionalized graphene. The polymerization proceeds exclusively on the grafted graphene, and patterned structures with high spatial resolution down to 3 μm could have been prepared. The composite exhibits enhanced efficiency of electrochemical doping compared to pristine graphene, unsymmetrical transport characteristic with very good hole-transporting properties and efficient electronic communication between the two materials. The covalent functionalization of graphene thus introduces advanced functionality to the material, broadening its scope of applications.

Keywords: Graphene, covalent functionalization, PEDOT, 2D heterostructures

1. INTRODUCTION

Reaching the ultimate potential of graphene [1,2] in multitude of fields requires means of on-demand tuning of its properties. [3] Covalent chemical functionalization [4,5] of the graphene monolayer provides merely unlimited space for targeted attachment of various moieties and thus manipulation of intrinsic parameters of the material. [6] The approach, however, is facing three crucial challenges on the way towards its goal: inducing chemical reaction, properly characterizing its product, and application of the chemical functional group in extending functionality of the material.

The long-known graphene grafting with diazonium-derived radicals [7-9] has been recently complemented by nucleophilic [10-13] and electrophilic substitution [14,15] methods on fluorinated and hydrogenated graphene, respectively, thus proving alternative for chemically incompatible species. The issue of characterization, conventionally dominated by Raman spectroscopy [16-18] and XPS, [19,20] was elaborated in detail by application of surface-specific and surface-enhanced versions of mass spectrometry, thermal programmed desorption, Raman spectroscopy and others. [11,21,22] These methods provided unambiguous experimental evidence for particular chemical moieties being grafted to the monolayer regardless the reaction employed by reporting on the mass and spectroscopic fingerprints of these species.

The modified surface was studied for chemoselective heterostructure formation. [23-25] The sulfonate-functionalized photolithographically patterned graphene was used to selectively promote oxidative polymerization of PEDOT and to stabilize the product.^[26] The reaction provided thin (<5 nm) hybrid material with down to micrometer scale resolution of the semiconducting polymer, extremely difficult to produce by other means, while preserving the differentiated hole/electron charge carrier mobilities and electrochromism.

2. RESULTS AND DISCUSSION

Graphene was synthesized by chemical vapour deposition (CVD) on copper foil, from which it can be transferred onto other substrates by copper-etching nitrocellulose assisted method. Due to the monolayer character of the CVD, the substrate has enormous effect on the reactivity of the material.^[27-29] Three mechanistically different procedures were employed to covalently introduce functional groups on the surface: radical diazonium grafting, nucleophilic substitution of fluorinated graphene and electrophilic substitution of partly hydrogenated graphene (**Figure 1**, see Methods for particular protocols). In the case of substitution reactions, the fluorination or hydrogenation can be regarded as primary activation of the material towards further modifications. It is important to note that the material is only partly fluorinated or hydrogenated - this has large impact on the reactivity in the subsequent transformations, because all the activating atoms introduced are statistically located in 'special' position such as allylic or benzylic. This fact thus enables nucleophilic substitution *via* allylic positions (S_N2' mechanism) or facile deprotonation of the hydrogenated graphene in 'benzylic' position. The three available mechanism to introduce functional groups to graphene are also extremely important with respect to chemical compatibility. For instance, the radical diazonium species are very reactive and do not tolerate strong nucleophiles and/or oxidizable species such as thiols. Finally, the versatility of graphene functionalization protocols also simplifies the preparation of specific molecules to be grafted on the monolayer, thus avoiding lengthy, tedious multi-step syntheses.

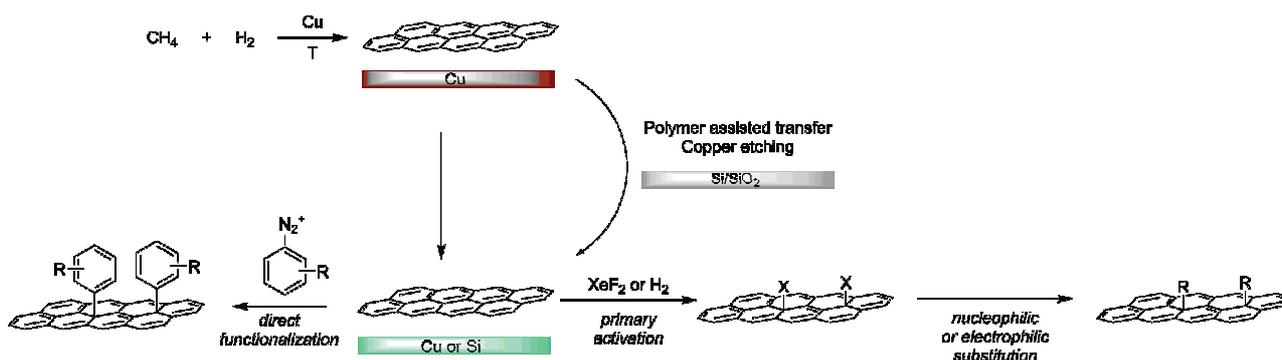


Figure 1 Scheme of graphene synthesis, transfer and functionalization according to different protocols

Performing on-surface reactions with CVD graphene requires also solid characterization of the reaction products. Due to the low amount of material in the monolayer, specific surface-oriented and surface-enhanced methods have to be used. The traditional approach involves measuring Raman and XPS spectra, however this information is largely insufficient to draw any conclusions about covalent grafting, since Raman spectra only report increasing or decreasing amounts of defects in the otherwise perfect 2D crystal (D mode) without any indication about their nature, and XPS provides elemental composition of the surface layer regardless if originating from functionalization or contamination.

We have thus engaged ourselves in extending the pool of available characterization techniques for graphene covalent functionalization (**Figure 2**). We have used surface-enhanced versions of Raman (SERS) and infrared spectroscopy (SEIRA) and mass spectrometry (SELDI) which provide characteristic bands for particular functional groups and mass of the grafted species, thus confirming structural integrity of the introduced moieties. The results are further supported by atomic force microscopy (AFM) which rules out the possibility of formation of functional multilayers, thermal programmed desorption (TPD) which eliminates the possibility of physisorption, and scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM/EDX) providing very high spatial resolution in mapping the surface morphology and elemental composition.

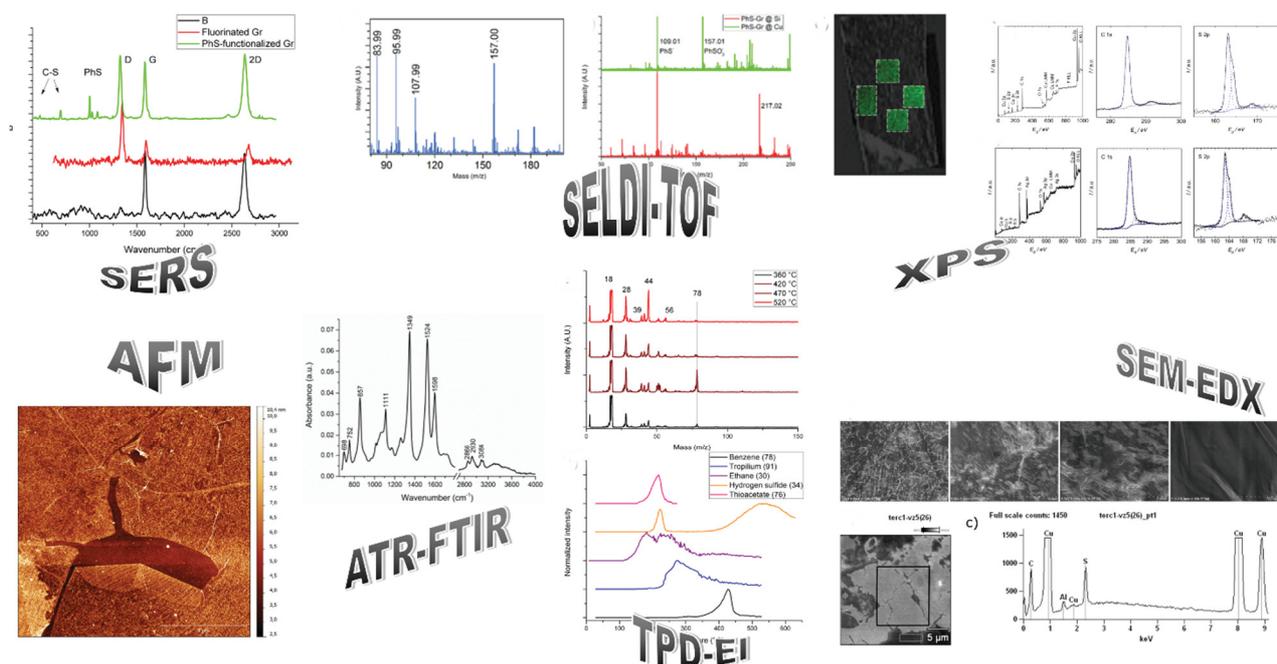


Figure 2 Overview of available characterization methods for graphene functionalization

With these tools in hand, we have advanced towards selective formation of functional hybrid heterostructures. First, we have functionalized the monolayer graphene with 4-sulfonylphenyl groups. This material is to some extent resembling PSS, common polymer used to stabilize PEDOT in aqueous solutions. Therefore we have employed this material in polymerization reaction of 3,4-ethylenedioxy-thiophene (EDOT). The sulfonyl group is catalysing the oxidative coupling and also compensate the positive charge of PEDOT chains thus stabilizing it. Very high spatial resolution of the reaction has been found, practically being limited only by the photolithography resolution (3 μm). The formed composite was studied by spectroelectrochemical methods and also employed in a prototypical device - transistor. It was found that the hybrid is electrochromic, enable higher negative charging of graphene and exhibit hole conducting/electron blocking properties with hole mobility higher than electron mobility by two orders of magnitude.

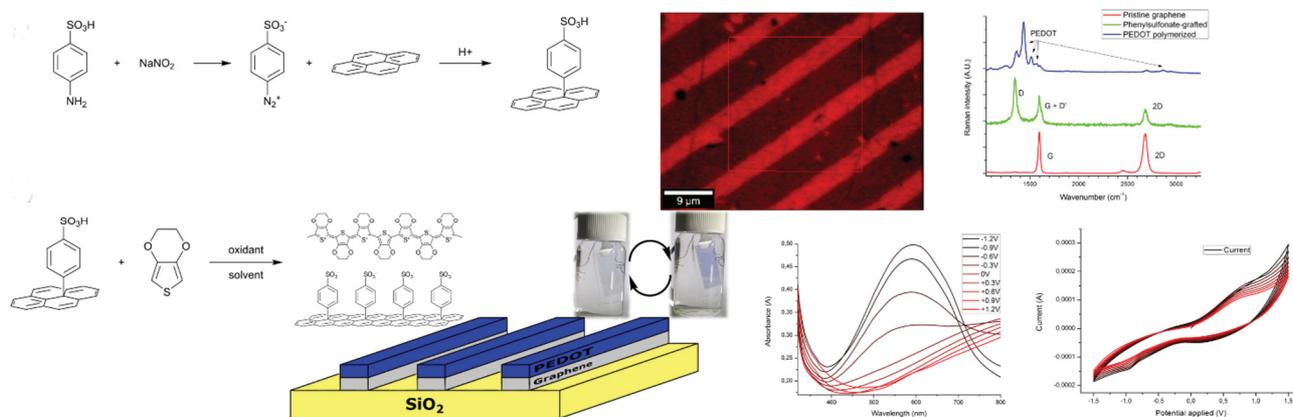


Figure 3 Scheme of selective PEDOT polymerization on functionalized patterned graphene

3. METHODS

3.1. Graphene growth and transfer

Graphene was grown on copper by CVD and transferred to SiO₂/Si substrates, as described previously. [30] In brief, a polycrystalline copper foil was annealed for 20 min at 1000 °C in hydrogen. Graphene was then grown from 1 sccm CH₄ for 35 min and then annealed for another five minutes in H₂ atmosphere. The sample was then cooled to room temperature and transferred to a Si/SiO₂ substrate using the nitrocellulose-based technique. [31]

3.2. Photolithography - graphene patterns

Graphene on substrate was covered with photoresist AZ 6632 by spincoating, aligned with the mask, exposed to the mercury short arc lamp light and developed by the AZ726MIF. Then graphene was etched by oxygen plasma and the polymer mask was removed by the NI555 stripper. Samples were then washed with *i*-propanol and dried in a stream of nitrogen.

3.3. Fluorination of graphene

The fluorination was performed in a self-built apparatus. The sample on a substrate was placed in a vacuum chamber containing blank Si/SiO₂ wafer, evacuated to $\approx 2 \cdot 10^{-4}$ mbar, then isolated from the pump and connected to the solid XeF₂ (Aldrich, 99.99%) reservoir. When the pressure reached 8 mbar (about 60 s), the valve to the reservoir was closed and the system was evacuated to remove residual XeF₂ vapours and then slowly ventilated to the ambient atmosphere.

3.4. Nucleophilic substitution

For volatile nucleophiles, the fluorinated graphene sample (about 1 cm² on a substrate) was placed in a vial (≈ 40 mL). The chamber was then evacuated with a membrane pump and refilled with argon (>99.95%) three times to remove oxygen. The nucleophile was then introduced via a Hamilton syringe through a septum on the bottom of the chamber without direct contact with the fluorinated graphene. The reaction thus proceeds only with the nucleophiles in the gas phase. After exposure for 2 h at r.t., the excess of the reagent was removed using a membrane pump and the samples were further exposed to high vacuum (10^{-5} mbar) for 15 min. Solid nucleophiles were dissolved in methanol (50 mg in 10 mL) in presence of a base, fluorinated graphene was immersed in it for 30 min at r.t. Then, the sample was removed and thoroughly washed with water, methanol and dichloromethane. Non-commercial thiols were synthesized from the corresponding isothiuronium salts.

3.5. Graphene hydrogenation

The samples were hydrogenated in a high-pressure autoclave (Berghof HR-100). Prior to the hydrogenation process, the vessel was flushed several times with hydrogen to remove air. Thereafter, the autoclave was filled with H₂ at a pressure of 5 bar at room temperature before the temperature was elevated to 200 °C. The reaction was carried out for 2 hours at roughly 8 bar and the samples were then cooled to room temperature.

3.6. Electrophilic substitution

Benzyl bromide (100 μ L, 0.84 mmol) was diluted in 5 mL of dimethylsulfoxide (DMSO; spectroscopy grade), and 200 mg of anhydrous potassium carbonate (K₂CO₃; 1.45 mmol, 1.7 eq.) was added. Hydrogenated graphene on a substrate was immersed in for two hours at room temperature, and after, the sample was removed and thoroughly washed with deionized water and MeOH (spectroscopy grade, 10 \times 5 mL each) and finally dried in a stream of argon.

3.7. Diazonium grafting

Commercial diazonium salts were used if available. Diazonium salts were diluted in deionized water ($>18 \text{ M}\Omega \text{ cm}^{-1}$) or mixture of deionized water and acetonitrile (7:3) to help the solubility to give 5 mM solution. Graphene on a substrate was immersed into the solution for 2 hours, then removed and thoroughly washed with water and spectroscopy grade methanol. Non-commercial diazonium salts were synthesized according to the following protocol: an aromatic amine (75 μmol) was diluted or suspended in 5 mL of the mixture of deionized water/acetonitrile 7:3 and 1.1 eq. of NaNO_2 was added. The reaction mixture was then acidified by 1M HCl to reach pH of $\sim 3-4$ when graphene on a substrate was immersed in. Reaction was carried out for 30 min at r.t., then the sample was removed and thoroughly washed with deionized water and methanol (spectroscopy grade).

3.8. EDOT polymerization

In a 50 mL beaker 60 mg of $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ was diluted either in 25 mL of acetonitrile or 10 mL of propylene carbonate and 32 mg of 3,4-ethylenedioxythiophene was added via syringe while stirring. In the case of acetonitrile solutions, deep blue color evolved immediately. Functionalized graphene on substrate was then immersed in the solution for a given time (20 - 80 minutes) at room temperature, then removed and washed thoroughly with UV-VIS grade methanol.

4. CONCLUSIONS

We have demonstrated three different mechanisms for introduction of broad range of chemical functional groups to the monolayer CVD graphene. These protocols allow to avoid potential chemical incompatibilities of functional groups with the reactive species. For the characterization of the on-surface reaction products, we have demonstrated the feasibility of a whole set of suitable spectroscopic and spectrometric techniques which, when combined, provide unambiguous evidence for the particular surface grafting. Finally, the established protocols were employed in preparation of hybrid graphene composite with PEDOT, which was selectively grown on a photolithographically patterned pre-functionalized monolayer. In this way, semiconducting electrochromic device has been prepared with micrometric resolution, which is extremely difficult to prepare by other methods.

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